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The Reactions of Hydroquinone and Derivatives

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The literature relating to the history, occurrence, physical properties, manufacture, and uses of hydroquinone has been reviewed recently in an excellent fashion elsewhere (1). In the present discussion, attention will be directed to the more important chemical reactions of hydroquinone, the use of hydroquinone as an intermediate in transformations of possible commercial value, and a brief survey of some hydroquinone derivatives of special interest.

Hydroquinone readily undergoes oxidation to quinone through use of various oxidizing agents as, for example, ferric chloride and dichromate solutions. A good preparative method for quinone involves oxidation of hydroquinone in dilute aqueous sulfuric acid, using sodium chlorate in the presence of vanadium pentoxide as catalyst (92-96% yield) (2) or potassium bromate (quantitative) (3). Hydroquinone may be determined volumetrically by oxidation with ceric sulfate using diphenyl amine (4) or ferrous phenanthroline (5) as indicator. When equimolecular quantities of hydroquinone and quinone are mixed in an organic solvent such as ethyl alcohol, the molecular complex known as quinhydrone separates as a dark green crystalline solid. Quinhydrone yields hydroquinone on reduction and quinone on oxidation. In solution it dissociates into the components to reach equilibrium. The rapid, quantitative, and reversible oxidation-reduction relationship of the quinone-hydroquinone system has been applied as the basis for pH measurements as the quinhydrone electrode.

Hydroquinone may be catalytically hydrogenated to produce a mixture of two stereoisomeric forms of 1,4-cyclohexanediol, commonly called quinitol. The *cis* (M.P. 111-112 C) and *trans* (141-141.5 C) cyclohexanediols have been separated by crystallization from the diacetates (6).

Hydroquinone is easily monosulfonated by warming to 50 C with concentrated sulfuric acid. Disulfonation is accomplished by heating at 100 C for eight hours with concentrated sulfuric acid or for two hours with oleum (7). The ammonium salts of hydroquinone monosulfonic acid and 2,5-hydroquinone disulfonic acid have been prepared by the reaction of hydroquinone with aminosulfonic acid (sulfamic acid) (8). Chlorination of hydroquinone gives rise to mixtures of chlorinated hydroquinones or quinones according to the reaction conditions. The patent literature describes the chlorination of hydroquinone in concentrated hydrochloric acid (9) and in carbon tetrachloride (10) to yield

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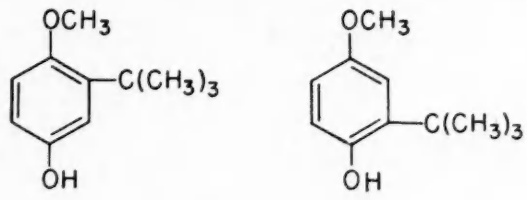
the possible chlorinated hydroquinones. A recent Russian paper (11) describes the use of dioxane dibromide to prepare either monobromohydroquinone or 2,6-dibromohydroquinone in 90% yield. Monoiodohydroquinone has been synthesized indirectly through oxidation of 3-iodo-4-aminophenol (4-amino-3-iodophenol) (12).

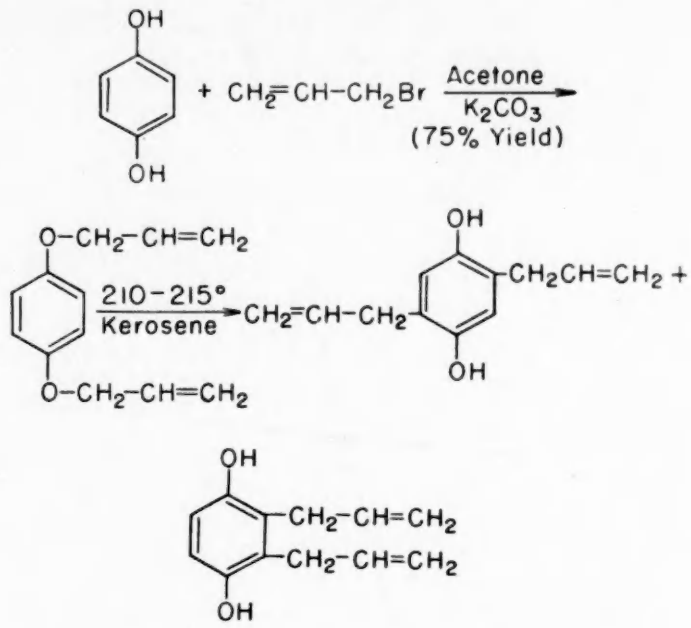
Dialkyl ethers of hydroquinone may be prepared in high yields by reaction of hydroquinone with an alkyl halide or sulfate under alkaline conditions. Some dialkyl ethers so obtained, particularly dimethyl, diethyl, and di-*n*-butyl ether, are of interest because, through nitration and reduction to aminohydroquinone ethers, they become useful dye intermediates. Hydroquinone diphenyl ether is formed by heating a phenolate salt with *p*-dibromobenzene to 180-200 C in the presence of copper powder (13).

The preparation of the monoethers of hydroquinone is subject to the disadvantage of simultaneous dietherification. However, the proportion of diether can be minimized in most cases by proper control of reaction conditions. Hydroquinone monomethyl-(*p*-methoxyphenol) and monobenzyl ethers [*p*-(benzyloxy) phenol] are of interest as antioxidants. Also, two tertiary alkyl-4-hydroxyanisoles have been described as antioxidants (14) (15). Monoetherification of hydroquinone, followed by alkylation with isobutylene or tertiary butyl alcohol, gives rise to a very useful antioxidant, namely, butylated hydroxyanisole (BHA), a mixture of the following isomers:

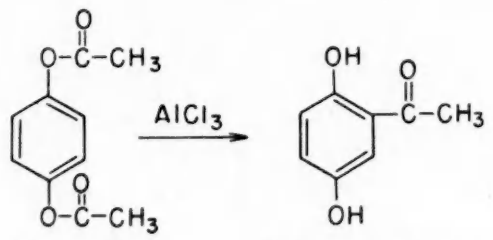


BHA possesses the valuable property, when incorporated in animal fats and shortenings, of imparting its antioxidant effect to the final food product (15) (16) (17), and has been approved by the U. S. Department of Agriculture, Meat Inspection Division, for that purpose.

Hydroquinone allyl ethers undergo the Claisen rearrangement to produce nuclear allyl derivatives, 2,3-diallylhydroquinone and 2,5-diallylhydroquinone in approximately equal amounts (18).



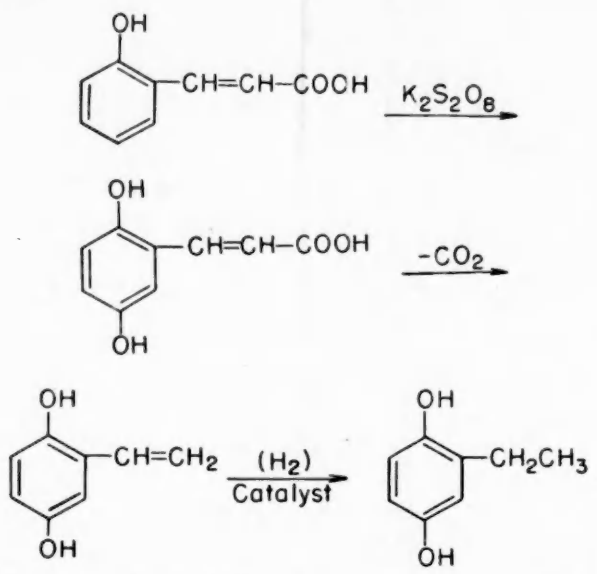
Hydroquinone may be converted into diesters by reaction with acid anhydrides or acid halides. As in monoetherification, the isolation of the monoesters in high yield is more difficult. Hydroquinone diesters rearrange according to the Fries reaction to form 2,5-dihydroxyphenyl alkyl ketones. For example, hydroquinone diacetate (*p*-phenylene diacetate) has been treated with aluminum chloride to form quinacetophenone (2,5-dihydroxyacetophenone) in 90% yield; one acetyl group is lost in the process (19).



Quinacetophenone

Many mononuclearly substituted alkyl hydroquinones have been prepared (20). The monomethyl derivative, toluhydroquinone, may be prepared by pyrolusite oxidation of *o*-toluidine under

the same general conditions used for the manufacture of hydroquinone. As described recently (21) (22), vinyl hydroquinone was synthesized indirectly through persulfate oxidation of *o*-coumaric acid, followed by decarboxylation. The vinyl hydroquinone obtained was hydrogenated to monoethyl hydroquinone.



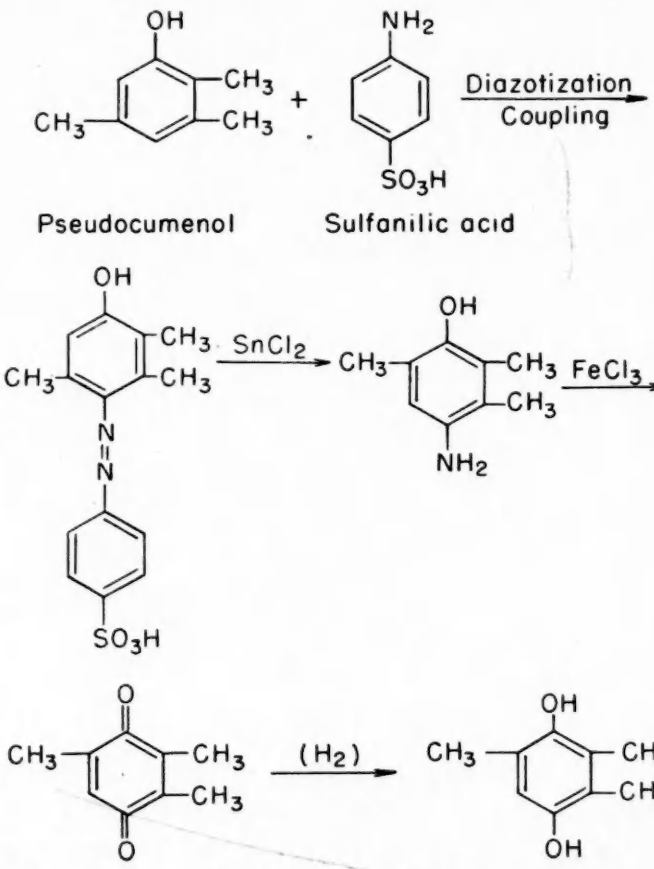
n-Alkyl derivatives may be prepared by reducing hydroquinones substituted with acyl or *n*-unsaturated groups (23).

Vinyl hydroquinone polymers possess the interesting property of exchanging electrons with their environment, and can be used to conduct oxidation and reduction reactions by methods employed with ion-exchange resins (24).

Hydroquinone may also be directly alkylated in the nucleus by means of an alcohol or olefin in the presence of a catalyst. Monoisopropyl hydroquinone was first prepared by direct nuclear alkylation in 1939 from hydroquinone and isopropyl alcohol, using hydrofluoric acid as catalyst (25). When an excess of isopropyl alcohol was used, the product was 2,4,6-triisopropylphenol (82.7% yield) rather than higher alkylated hydroquinones. The product of catalytic nuclear alkylation of hydroquinone under ordinary conditions with isobutylene or tertiary butyl alcohol is 2,5-ditertiary butyl hydroquinone (26). This compound has found several useful applications as a polymerization inhibitor in the manufacture of plastics, an antioxidant for vegetable fats and oils, and in ultraviolet stabilization of rubber and synthetic elastomers. Higher alkylated hydroquinones may be prepared by condensing alkenes containing eight to eighteen carbon atoms with hydroquinone in the presence of a condensing agent such as sulfuric acid, zinc chloride, or aluminum chloride. These compounds are useful as gelling agents with liquid aliphatic hydrocarbons and certain chlorinated aliphatic hydrocarbons (27).

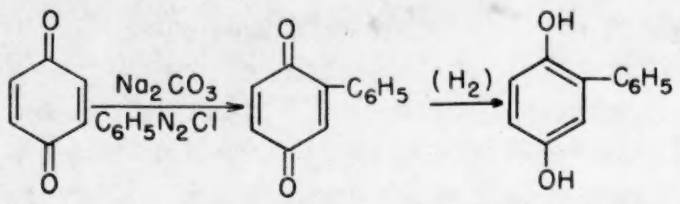
Several of the polymethylated hydroquinones are of interest in the synthesis of tocopherols. For example, *dl*-α-tocopherol, which is about 75% as active as the natural *d*-α-tocopherol, has been prepared by condensation of trimethyl hydroquinone with phytyl bromide (28).

Trimethyl hydroquinone (pseudocumohydroquinone) may be prepared as described by Smith and co-workers (29), starting from pseudocumenol.



The yield of trimethyl quinone (pseudocumoquinone) from the pseudocumenol was 90-95%.

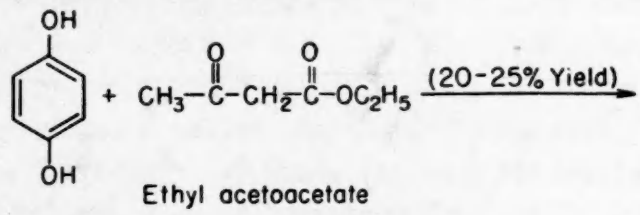
Nuclearly substituted aryl hydroquinones are usually prepared by reaction of a quinone with a diazonium salt, followed by reduction.



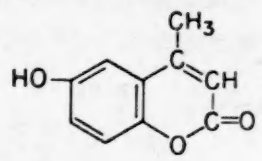
Phenylquinone Phenylhydroquinone

Phenylquinone and the corresponding hydroquinone, which is an effective oil-soluble antioxidant, may be obtained in nearly quantitative yields by this method. Other aryl derivatives of hydroquinone have been so prepared (30) (31).

The Von Pechmann method for preparing substituted coumarins may be applied to hydroquinone and many of its derivatives (32).



Ethyl acetoacetate



4-Methyl-6-hydroxycoumarin

(To be concluded)

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